

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup>:</b> <b>C08F 4/16, 10/00, B01J 37/02</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 95/07305</b> <b>(43) International Publication Date:</b> 16 March 1995 (16.03.95)
<b>(21) International Application Number:</b> PCT/FI94/00394 <b>(22) International Filing Date:</b> 6 September 1994 (06.09.94)  <b>(30) Priority Data:</b> 933998 10 September 1993 (10.09.93) FI  <b>(71) Applicant:</b> NESTE OY [FI/FI]; Keilaniemi, FIN-02150 Espoo (FI).  <b>(72) Inventors:</b> KNUUTTILA, Hilka; Torpparintie 4, FIN-06400 Porvoo (FI). SORMUNEN, Pekka; Ordurpvej 102, 4.th, DK-2920 Charlottenlund (DK). IISKOLA, Eero; Linnankoskenkatu 15 A 1, FIN-06100 Porvoo (FI). LAKO-MAA, Eeva-Liisa; Soukanahde 7 F 116, FIN-02630 Espoo (FI). HOKKANEN, Harri; Ketokiventie 3 as. 5, FIN-00710 Helsinki (FI).  <b>(74) Agents:</b> LAINE, Seppo et al.; Seppo Laine Oy, Lönnrotinkatu 19 A, FIN-00120 Helsinki (FI).		<b>(81) Designated States:</b> AU, BR, CA, CN, JP, KR, NO, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> CATALYST FOR POLYMERIZATION OF ETHYLENE  <b>(57) Abstract</b>  The present invention concerns a heterogeneous catalyst for polymerization of olefins. The catalysts include at least one group IVa metal compound on a solid inorganic oxidic support. According to the invention the catalysts are prepared by vapourizing at least one solid group IVa metal halide compound and routing the vapour of the metal halide compound into a reaction chamber, wherein the vapour is reacted with the support at a temperature of about 250 to about 450 °C in order to bind said metal halide compound to said support. Any metal compound not bound to said support as well as any volatile reaction products emanating from the reaction between said metal halide compound and said support are then removed from the reaction chamber in the vapour phase. Optionally the product obtained is treated with an organic aluminum compound to increase the catalytic activity of said catalyst. The catalysts thus prepared are very well suited for polymerization of ethylene or copolymerization of ethylene with other alfa-olefins, such as propylene, butylene, 4-methyl-1-pentene and hexene. A polymerization process employing the novel catalyst will provide products of the Ultra High Molecular Weight-type (UHMWPE) having very broad MWD.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

## CATALYST FOR POLYMERIZATION OF ETHYLENE

### Background of the Invention

#### 5 Field of the Invention

The present invention relates to a process for preparing polymerization catalysts for olefins. Said catalysts are particularly suited for the polymerization of ethylene.

10 The present novel polymerization catalysts comprise a support consisting of an inorganic oxide or a mixture of inorganic oxides, the surface of said support having a group IVa metal compound bound to its surface.

Furthermore, the present invention concerns a process for the homo- and copolymerization of  
15 olefins, in particular ethylene, in the presence of a heterogeneous catalyst.

### Description of Related Art

It is known in the art that oligomerisation and polymerisation of ethylene can be catalysed by  
20 compositions comprising vanadium, titanium and/or zirconium halides and possibly other components on an inorganic oxidic support. Typically, these heterogeneous catalysts are prepared by stirring the support, for instance silica or alumina, in a solution of the transition metal compound(s) used, evaporating the product and, if desired, suspending it in a solution of a suitable cocatalyst compound, such as an organo-Al compound, before polymerization.

25 The prior art is hampered by considerable problems. For example, the use of solvents makes the processes complex because additional process steps (evaporation) are needed for separating the solvents from the products. Furthermore, as far as the preparation of Zr- and Hf-containing catalysts using chlorides is concerned, the reagents are solid substances, which  
30 are poorly soluble in non-polar solvents. Therefore, polar solvents, such as water and alcohols, will have to be used as reaction media. These solvents are, however, known to impair the activity of the catalysts.

### **Summary of the Invention**

It is an object of the present invention to eliminate the problems of the prior art and to provide novel zirconium chloride -based catalysts, as well as novel processes for preparing supported group IVa metal catalysts, and for polymerization of olefins.

The present invention is based on the concept of evaporating the group IVa metal reagent, preferably a group IVa metal halide, separately from the support and routing the vapour into a reaction chamber, wherein the vapour is reacted with the support. During the reaction, the support is kept at a temperature which is higher than the condensation temperature of the vapour and simultaneously so high as to achieve the thermal activation energy necessary for establishing chemical bonds between the metal compound and the support (chemisorption of the metal compound).

### **Brief Description of the Drawings**

Figures 1 and 2 show the binding of  $ZrCl_4$  as a function of the preheating temperature of the support,

Figure 3 shows the activity of the catalysts as a function of the Al/Zr molar ratio,

Figure 4 indicates the change in Zr concentration when silica preheated at 300 °C is pretreated with  $TiCl_4$  at 175 - 300 °C,

Figure 5 shows the XRD patterns for  $ZrCl_4$ /silica catalysts treated at different temperatures, and

Figure 6 shows the molecular weight distributions of PE produced by  $ZrCl_4$  on silica with two different hydrogen/ethylene ratios.

### **Detailed Description of the Invention**

The present catalysts comprise compounds, in particular halides, of one or more group IVa metals deposited from the vapour phase on an oxidic support. Should the catalysts contain only one metal compound, then that compound is selected from the group consisting of the fluorides, chlorides, bromides and iodides of zirconium and hafnium. Likewise, if there are

several metal compounds, then at least one of those compounds is selected from the group of compounds listed above. The oxidic supports are preferably selected from the group consisting of silica and alumina.

- 5 According to a preferred embodiment, the novel zirconium chloride catalyst provided by the present invention comprises an essentially amorphous zirconium compound of the formula  $ZrY_x$ , wherein Y is a halo, preferably chloro or bromo, and x is 2 or 3, on an oxidic support selected from the group consisting of silica and alumina. From instrumental analysis of the catalysts it appears that, for instance, the zirconium chloride has reacted with the hydroxyl  
10 groups on the surface of the support, resulting in direct chlorination of the OH groups. Therefore, depending on whether the zirconium chloride molecule has reacted with one or two OH groups, the formula of the zirconium species bound to the support is either  $ZrCl_3$  or  $ZrCl_2$ . Because of the reaction, HY is released. The novel catalyst is capable of catalyzing the homo- and copolymerization of ethylene. According to one embodiment, the catalysts are  
15 capable of catalyzing ethylene polymerization in the gas phase at an increased pressure of at least 2000 kPa, producing polyethylene having a broad molecular weight distribution, the polydispersity being at least 15.

- According to the process of the present invention, the catalysts are prepared by vaporizing  
20 suitable group IVa metal compounds and reacting the vapours with an oxidic support so as to deposit them thereon. For the vaporization of zirconium and hafnium it is particularly preferred to use solid halides, in particular halides selected from the group consisting of  $ZrCl_4$ ,  $ZrBr_4$ ,  $HfCl_4$  and  $HfBr_4$ . It has surprisingly been found that many organic zirconium and hafnium compounds, which have suitable boiling points, cannot be used in the present  
25 invention because they tend to decompose in the vapour phase. However, the halides of the same elements, which are solid substances at ambient temperature, are readily vaporized at temperatures above 250 °C and are stable up to 500 °C. One preferred embodiment of the invention comprises providing an amorphous group IVa metal compound on silica support. According to that embodiment the temperature should not be allowed to rise above 350 °C  
30 during the reaction between the metal halide, in particular the metal chloride, and the support, because, e.g., the zirconium chloride species ( $ZrCl_3$  and  $ZrCl_2$ ) will start to form crystallites of the formula  $ZrO_2$  on the surface of the support at temperatures over about 350

°C. The crystallites will impair the activity of the catalysts. At temperatures of about 600 °C, the catalysts prepared on silica support become practically inactivated. On alumina supports, higher reaction temperatures can be used.

5 As mentioned above, the catalysts prepared can contain more than one group IVa metal compound. One of the compounds is always zirconium or hafnium fluoride, chloride, bromide or iodide, respectively, whereas the second and third compounds may comprise a hafnium, zirconium or titanium halide. Titanium halides can be bound to the support from vaporized titanium halides, such as  $\text{TiCl}_4$ , or from organometal compounds which are  
10 composed by reacting them with hydrohalo acids to form the corresponding halides on the support. Of the organic titanium compounds, in particular the alkoxides, such as the isopropoxide and the isobutoxide derivatives, should be mentioned.

Of the above-mentioned halogen compounds,  $\text{ZrCl}_4$  and  $\text{HfCl}_4$  are typically vaporized at a  
15 temperature in the range from 250 to 350 °C, in particular 260 °C to 320 °C, whereas  $\text{TiCl}_4$  is vaporized at a temperature above 25 °C.

The reagents,  $\text{ZrCl}_4$ ,  $\text{HfCl}_4$  and  $\text{TiCl}_4$  compete with each other for the same bonding sites. That is the reason why the binding order of the reagents has an effect on the saturation level  
20 (cf. below) in addition to the preheat temperature of the support and the chemisorption temperature. If, for instance,  $\text{ZrCl}_4$  is first processed to silica (calcined at 300 °C) and then  $\text{TiCl}_4$ , in a particular embodiment some 1 wt-% of Ti and 6 wt-% of Zr are bound to the support. However, if the pulsing order is reversed,  $\text{ZrCl}_4$  removes all Ti from the support and the Zr content becomes as high as 9.3 wt-%. Thus, it appears that  $\text{TiCl}_4$  creates new  
25 binding sites for  $\text{ZrCl}_4$  (cf. the chemical treatment with  $\text{AlCl}_3$  described below). The vapour pressure of  $\text{HfCl}_4$  and  $\text{ZrCl}_4$  can be regulated to the same level, and these reagents can also be brought to the support simultaneously, although a more precise metal content regulation is achieved by alternate pulsing of the reagents. It is also possible to vaporize two of the reagents simultaneously.

30

According to a preferred embodiment of the invention, the catalyst preparation comprises the following stages:

1) Pretreatment of the oxidic support, 2) vaporization of the reactant(s) and binding of it (them) to the support surface, 3) flushing with an inert gas and 4) an optional treatment of the catalyst with organic aluminium compounds.

- 5 According to the invention all reagents for stages 1, 2 and 3 are brought into the reaction chamber in the vapour phase, typically one component at a time.

In the first stage of the process, the support can be subjected to a pretreatment at elevated temperatures prior to the actual binding reaction. The heat treatment of the support can be applied to modify the number and character of the OH groups on the support and, thereby, the amount of metal species bound. The maximum temperature of the preheating process of silica supports is about 450 °C if  $ZrCl_4$  is to be bound thereto. Alumina supports can be preheated up to temperatures in the range of 800 to 900 °C.

- 15 An elevated pretreatment temperature reduces the number of excess OH groups and diminishes side reactions catalyzed by acid sites. The heat pretreatment is carried out for 1 to 40 h, preferably for 2 to 24 hours.

Instead of, or in addition to heating, the support can also be pretreated by contacting it with suitable compounds which will modify its surface in an advantageous way. Thus, the silica support can be treated with aluminium compounds. By reacting aluminium chloride and water vapour with silica, an  $Al_2O_3$  layer can be formed which prevents the formation of  $ZrO_2$  crystallites onto the surface of the support. In addition to aluminium chloride organic aluminium compounds can be used. The following examples may be mentioned: TMA (trimethylaluminium), TEA (triethylaluminium), DEALOX (diethylaluminium ethoxide, TEB (triethylboron) TIBA (triisobutylaluminium), EADC (ethylaluminium dichloride) and MAO (methylalumoxane)

In the second stage of the process, vaporized reagent(s) is (are) chemisorbed to the support by contacting the reagent vapours with the support. The vapour pressure of the vaporized group IVa metal compound is kept sufficiently high during the process and the duration of interaction with the support material surface sufficiently long so as to achieve saturation or,

preferably supersaturation, with the active material or its precursor, respectively, at the bonding sites of the support material. The partial pressure of the vaporized reagent is typically in the range from about 0,010 to about 95 kPa. Lower pressures will require longer reaction times. It is particularly preferred to use a partial pressure of at least 1 kPa.  $ZrCl_4$  and  $HfCl_4$  are preferably vaporized at temperatures in the range of 260 to 320 °C which corresponds to partial vapor pressures in the range of about 5 to 50 kPa (for  $ZrCl_4$ ) and 10 to 95 kPa (for  $HfCl_4$ ).  $TiCl_4$  is preferably vaporized at temperatures in the range of about 23 °C to 70 °C (corresponding to partial pressures of about 1 to 15 kPa). The proportion of excess active material used in relation to the concentration necessary to achieve complete saturation of all available bonding sites on the support material surface (customarily called a monolayer coverage) is typically 1- to 100-fold, preferably 1- to 3-fold. The amount of the group IVa metal compound necessary for a monolayer coverage can be calculated from the area of the support determined with the help of, e.g., the BET method, and from the known molecular structure of the support.

According to a preferred embodiment, the reaction temperature must not fall below the temperature necessary for the evaporation of the reagent; otherwise, condensation of the reagent could occur. Further, the reagent must not be allowed to condense on its way to the reaction chamber. Therefore, its temperature must not be allowed to fall below the reaction temperature. The group IVa compound and the operating temperature must be selected so as to avoid the decomposition of the metal compound or a possible condensation of its decomposition products.

Using experimental methods it is possible to determine a temperature range, or temperature span, in which the reaction is most advantageously carried out. As explained above, if silica is used as support, the second stage of the process is preferably carried out at a temperature in the range from about 250 to about 350 °C, in particular about 260 to about 320 °C. The lower limit of the given temperature span is determined by the condensation temperature of the group IVa compound to be evaporated at the employed partial vacuum and by the activation energy necessary for establishing a desired surface bond. The upper limit is determined by the temperature at which the transition metal compound chemisorbed on the support will start to form crystallites, which are catalytically less active.



The reaction between the catalytically active material or its compound and the support can be carried out at ambient pressure, or alternatively, at overpressure. Preferably, the reaction is, however, carried out in a partial vacuum. Typically, the operating pressure of the process lies in the range from about 0.1 to about 1000 mbar (0,01 kPa to 100 kPa), preferably in the range from about 1 to about 100 mbar (0,1 kPa to 10 kPa). Also pre- and posttreatment steps, if any, are preferably carried out in partial vacuum. A benefit gained from the use of a partial vacuum is that the reaction space is kept cleaner and the diffusion rate is increased. The reaction time is not particularly critical as long as it is sufficient to allow the evaporated reagent to interact with all available binding sites of the support. Thus, in laboratory conditions the reaction time can be selected, for instance, in the range from about 1 min to 25 hours. Even shorter or longer periods of time are possible, depending on the intensity of the reaction between the reagent and the support and on the amount of the support. Conventionally a reaction time of some minutes up to 10 hours is sufficient for processing a 5 to 20 g amount of the support material.

The vaporized transition compound can be introduced into the reaction space as such, or alternatively, using an inert carrier gas such as nitrogen or a noble gas. Preferably, a protective gas atmosphere formed by an inert gas is used, the same inert gas being used as the carrier gas for the transition metal vapour.

Any unreacted transition metal reagent and the side products of the reaction between the metal and the support (HCl and organic residues of the reagent, for instance) are removed from the reaction space in the vapour phase and preferably at the reaction temperature (to avoid potential condensation problems). The chemisorption reaction is therefore followed by a nitrogen purge at the reaction temperature to remove unreacted reagent and released HCl.

After the binding of the transition metal catalytically active species to the support and prior to being used for polymerization, the catalyst can be modified, i.e. preactivated, by adding conventional organometal compounds, in particular Al-alkyl compounds typically used as cocatalysts. Suitable organometal compounds are, for example, TMA (trimethylaluminium), TEA (triethylaluminium), DEALOX (diethylaluminium ethoxide, TEB (triethylboron) TIBA (triisobutylaluminium), EADC (ethylaluminium dichloride) and MAO (methylalumoxane), to

mention a few. TMA, TEA, TIBA and DEALOX are considered to be particularly advantageous for the purpose of the present invention.

5 The reaction between the support containing the catalytically active transition metal species and the organometal compound is carried out by suspending the support in a solvent containing the suitable cocatalyst compound.

The cocatalyst may of course also be added to the polymerization reactor, as known per se. In that case, the catalysts are transferred in nitrogen atmosphere from the reaction chamber  
10 for cocatalyst addition and polymerization. If, however, the catalysts are preactivated as described above, no cocatalyst addition is needed during polymerization.

The polymerization is carried out according to known processes. Preferably, it is conducted at increased pressure in slurry or in vapor phase. The pressure depends on the process used.  
15 Typically, it varies from about 1,5 bar to 1000 bar (150 kPa to 100,000 kPa), preferably it is at least 5 bar (500 kPa). Thus, the pressure advantageously lies in the range from about 5 to 100 bar (500 kPa to 10,000 kPa), and in particular it is between about 10 and 75 bar (1,000 kPa - 7,500 kPa). The operational pressures of slurry processes are somewhat higher than those used in gas phase polymerization processes. The polymerization temperature is from  
20 about 20 to about 300 °C, preferably from about 50 to 275 °C. The partial hydrogen pressure is in the range from about 0,1 bar (10 kPa) to about 20 bar (2,000 kPa), preferably from about 0,5 bar (50 kPa) to about 10 bar (1,000 kPa).

The present invention provides significant benefits. The catalysts are readily prepared with  
25 the process according to the present invention. Since no solvents are used in the reaction of the transition metal and the support, no separate evaporation stage is needed, and the activity of the heterogeneous catalysts prepared is high. The catalyst systems are very well suited to polymerization of ethylene or copolymerization of ethylene with other  $\alpha$ -olefins, such as propylene, butylene, 4-methyl-1-pentene and hexene. They can be used in the gas phase or in  
30 slurry polymerization. Surprisingly, it has been found that the polymerization process employing the novel catalyst will provide products of the Ultra High Molecular Weight -type (UHMWPE) having very broad MWD and often having a bimodal molecular weight

distribution. The molecular weight of the HDPE produced is often over 350,000 at a hydrogen-to-ethylene partial pressure ratio of less than 0.20.  $MFR_{21.6}$  is 0.01 to 5, typically less than 1. The broad molecular weight distribution improves the mechanical properties of the polymers prepared, which can be used, in particular, as high-strength films and sheets.

- 5 By treating the catalyst prepared in the gas phase with aluminium alkyl compounds, the activity of the catalyst may be improved significantly.

Below, the invention will be examined in more detail with the aid of the following working examples.

10

### Experimental

#### A. Catalyst preparation

- 15 The processing equipment consists of a reaction chamber for 1 - 20 g of catalyst.  $ZrCl_4$  and  $HfCl_4$  were vapourized at 260 - 320 °C,  $TiCl_4$  at 25 °C. Chemisorption temperature was 150 - 550 °C for  $TiCl_4$  and 270 - 550 °C for  $ZrCl_4$  and  $HfCl_4$ . The selected metal halide was brought in nitrogen flow through heated lines to the reaction chamber and was reacted with the support (5 - 10 g) in nitrogen flow at a pressure of 50 - 1000 mbar for 1 to 3 hours. A  
20 purge with nitrogen for 1 to 3 hours was made after the reaction.

- The number of bonding sites of the preheated (300 - 900 °C) support can be determined by H-NMR, if necessary. The chloride compounds used react with isolated OH groups according to diffuse reflectance Fourier infra-red spectrometry (FTIR) measurement. The  
25 amount of reagent needed can thus be calculated, when the number of bonding sites is known. An overdose (1 to 2 times the number of the bonding sites) is vapourized. The saturation level of the metal concerned is not effected by the overdosing. The saturation level of the samples was monitored by determining the metal concentrations of samples taken from the upper part and the bottom of the solid support bed. Zr was determined by X-ray  
30 fluorescence spectrometry (XRF) or by instrumental neutron activation analysis (INAA). Hf and Ti were determined by INAA. UV-VIS spectrophotometry was used for Ti determinations. Chloride was determined in the samples by potentiometric titration. X-ray

diffraction (XRD) was used to determine if crystallization of  $\text{ZrCl}$  species to  $\text{ZrO}_2$  took place. Diffuse reflectance FTIR was used to analyze the bonding sites of  $\text{ZrCl}_4$  on silica.

### B. Polymerization conditions

5

Polymerizations were carried out in isobutane slurry, 1800 ml of 1-butane being added to a 3-l reactor. A catalyst and a cocatalyst were fed to the reactor under nitrogen pressure. Polymerization temperatures were 95 °C and 105 °C, and total pressures 3,100 and 4,100 kPa, respectively. Hydrogen was charged from a 500 ml bomb (pressure 5 bar) to the reactor at the beginning of the polymerization with ethylene flow. The reaction mixture was agitated first at 500 rpm, and after 10 minutes, the agitation speed was raised to 600 rpm, after a further 20 minutes, this was raised to 700 rpm.

### C. Cocatalyst addition

15

The influence of the amount of cocatalyst on the catalyst activity and melt flow rates of polymer solutions was studied by feeding various amounts of the cocatalyst to the reactor. The cocatalysts used comprised a 10 wt-% solution of triethylaluminium (TEA) in heptane (supplied by Schering) and methylalumoxane (MAO) in toluene (7.32 wt-% Al,  $\rho = 0.863 \text{ g/cm}^3$ ) (supplied by Texas Alkyl, Inc.). The  $\text{ZrCl}_4/\text{SiO}_2$  system was not active without cocatalyst.

### D. Catalyst modification with Al-alkyl-compounds

25

In some experiments an Al-alkyl compound was added straight to the catalyst and not to the reactor as normally. These modifications were done in inert atmosphere as follows: the catalyst was mixed with anhydrous pentane to obtain a slurry. An Al-alkyl solution was injected to the slurry and a colour change to yellow could immediately be observed. Mixing was continued for 2 hours at room temperature and after that the pentane was evaporated using standard Schlenk technique. Polymerization was carried out without cocatalysts.

30

**Example 1. Preparation of ZrCl<sub>4</sub> and HfCl<sub>4</sub> catalysts**

Under the experimental conditions described under section A above, a number of group IVa catalysts were prepared. Tables 1A to 1D indicate the results of the preparation processes.

5

**Table 1A. ZrCl<sub>4</sub> catalysts on silica or aluminium**

10

Sample	Support and pre-treatment T/°C	Zr wt-%
1	silica/300	6.8
2	silica/300	6.6
15	3 alumina/300	11
4	alumina/450	6.5
5	alumina/800	3.6
6	silica/300	6.9
7	silica/300	5.9, Hf 2.0 wt-%
20	8 silica/450	5.2
9	silica/300	- , Ti 3.8 wt-%

**Table 1B. ZrCl<sub>4</sub> catalysts on silica and further containing Ti**

5	Sample	Support and pre-treatment T/°C	Reagent + reaction-T/°C	Zr p-%	Ti p-%
10	10	silica 300	ZrCl <sub>4</sub> 300	5.9	1.0
			TiCl <sub>4</sub> 250		
	11	silica 300	TiCl <sub>4</sub> 250	9.3	< 0.1
			ZrCl <sub>4</sub> 300		
	12	silica 300	ZrCl <sub>4</sub> 300	7.7	0.3
			Ti-i-pro 210		
			HCl 210		
15	13	silica 300	Ti-i-pro 210	7.3	3.3
			HCl 210		
			ZrCl <sub>4</sub> 300		
	14	silica 300	ZrCl <sub>4</sub> 300	11	2.4
20			Ti-i-pro 200		
			HCl 200 -> 300		
			ZrCl <sub>4</sub> 300		
	15	silica 300	Ti-i-pro 200	10	1.4
			HCl 200->300		
25			ZrCl <sub>4</sub>		
			2 cycles, with intermittent N <sub>2</sub> treatment at 600 °C		
30	Ti-i-pro = titanium-isopropoxide				

**Table 1C. Binding of HfCl<sub>4</sub> and ZrCl<sub>4</sub> on silica preheated at 300 °C. Concentrations in percent by weight**

35	Sample	Preheating T °C/h	Reaction T °C/h	Concentration wt-%		
40				Hf	Zr	Cl
	16	300/16+3	Hf300/2	8.9	-	5.9
	17	300/16+3	Hf+Zr 300/2	3.2	5.0	6.1
				3.8	4.8	6.3
45	18	300/16+3	Hf/Zr 300/	1.4	6.8	6.3
			(5+5)x12	1.6	6.2	6.2
	19	300/16+3	Zr/Hf 300/	2.1	6.0	6.4
			(5+5)x12	2.6	5.9	6.3
	20	300/16+3	Hf+Zr 300/2	1.9	6.1	6.2
50				2.1	5.7	6.3

**Table 1D. Binding of HfCl<sub>4</sub> and ZrCl<sub>4</sub> on silica preheated at 300 °C. Concentrations in mmol/g**

Sample	Preheating T °C/h	Reaction T °C/h	Concentration (mmol/g)			
			Hf	Zr	Cl	Hf+Zr
16	300/16+3	Hf300/2	0.50	-	1.7	
17	300/16+3	Hf+Zr 300/2	0.18	0.55	1.7	0.73
			0.21	0.53	1.8	0.74
18	300/16+3	Hf/Zr 300/ (5+5)x12	0.08	0.75	1.8	0.83
			0.09	0.68	1.7	0.78
19	300/16+3	Zr/Hf 300/ (5+5)x12	0.12	0.66	1.8	0.78
			0.15	0.65	1.8	0.80
20	300/16+3	Hf+Zr 300/2	0.11	0.67	1.7	0.78
			0.12	0.62	1.8	0.74

ZrO<sub>2</sub> was formed according to XRD measurements (cf. figure 5), when ZrCl<sub>4</sub> reacted with silica preheated at higher than 450 °C or at reaction temperatures at or over 450 °C. Amorphous ZrCl<sub>x</sub> (x is 2 or 3) leads to better polymerization activity than crystalline ZrO<sub>2</sub> species.

From these tests, it appeared that the reagent ZrCl<sub>4</sub> contained a small amount of HfCl<sub>4</sub> as an impurity. The Hf:Zr ratio of the catalysts prepared remained constant (0.01) and was not dependent on the reaction conditions used. This is probably due to the similar vapour pressure of these two compounds.

The surface saturation level of Hf+Zr on silica preheated at 300 °C was 0.77 +/- 0.03 mmol/g (Table 1D).

Figures 1 and 2 show the binding of ZrCl<sub>4</sub> as a function of the preheating temperature of the support. It can be noted that the concentration of Zr can be regulated either by preheating the support or by varying the reaction temperature.

**Example 2. Ti with ZrCl<sub>4</sub>**

The ZrCl<sub>4</sub>/SiO<sub>2</sub> catalysts were treated with titanium compounds in order to modify the catalytic activity thereof, in particular to increase the amount of short-chained polymers.

5

Two different Ti reagents were used when processing Ti-Zr/silica catalysts: TiCl<sub>4</sub> and Ti-isopropoxide. TiCl<sub>4</sub> was vaporized at 25 °C and Ti-isopropoxide at 120 °C. Silica was preheated at 300 °C in all samples. Tables 2A and 2B show the saturation levels of Zr and Ti in samples processed in different ways. HCl gas was used to remove the ligand in

10 Ti-isopropoxide. Both Ti reagents can be used together with ZrCl<sub>4</sub>, but lower Ti saturation levels were measured when TiCl<sub>4</sub> was used instead of Ti-isopropoxide.

**I. TiCl<sub>4</sub>**

15 ZrCl<sub>4</sub> is capable of removing TiCl<sub>4</sub> on silica almost totally. ZrCl<sub>4</sub> must be bound to silica first and TiCl<sub>4</sub> after that at 300 °C in order to get Ti bound from TiCl<sub>4</sub>. The saturation level of Ti is 1.3 wt-% and part of Zr is released from the surface.

ZrCl<sub>4</sub> removes totally or partly both Ti and Hf bound from chlorides

20

The metal concentration of the catalysts can be regulated by varying the preheating temperature of the support and the reaction temperature



Table 2A. Binding of Ti and Zr on SiO<sub>2</sub> from TiCl<sub>4</sub> and ZrCl<sub>4</sub>

5	Sample	Pretreatment T °C/h	Reaction T °C/h	Concentration (p-%)		
				Zr	Ti	Cl
10	21	300/16+3	Ti 175/2	-	3.8	6.9
	22	300/16+3	Ti 300/2	-	3.2	4.7
	23	300/16+3	Zr 300/2	6.9	0.1	7.4
15	24	300/16+3	Ti 175/2	7.3	<0.05	7.4
	25	300/16+3	Ti 175/2	8.9	<0.05	7.0
	26	300/16+3	Zr 300/2	7.2	<0.05	7.0
20	27	300/16+3	Zr 300/2	3.5	1.5	5.4
	28	300/16+3	Ti 300/2	4.3	1.1	5.8
	29	300/16+3	Ti 175/2	6.8	0.06	6.4
25	30	300/16+3	Zr 300/2	8.1	0.04	6.6
	31	300/16+3	Ti 175/2	7.4	<0.05	6.9
	32	300/16+3	Ti 175--> 300/1.5			
30	33	300/16+3	Zr 300/2			
	34	300/16+3	Ti +Zr	5.1	0.7	6.1
	35	300/16+3	00/2	5.3	0.6	6.5
35	36	300/16+3	Ti 300/2	6.0	0.09	6.3
	37	300/16+3	Zr 300/2	6.1	0.07	6.6
	38	300/16+3				

It appears from the results that the TiCl<sub>4</sub> treatment of the silica surface obviously opens part of the hydrogen bonded OH groups, thus providing increased amounts of bonding sites to ZrCl<sub>4</sub> as compared with plain silica. Fig. 4 presents the change in Zr concentration when silica preheated at 300 °C is pretreated with TiCl<sub>4</sub> at 175 - 300 °C.

## II. Ti-isopropoxide

The saturation level of Ti on silica preheated at 300 °C was 3.3 wt-%. HCl can be used to remove the organic part bound to Ti. Ti itself was not released with HCl pulsing at 210 - 300 °C. Neither was Ti released when ZrCl<sub>4</sub> was bound after HCl treatment. Isolated OH groups and part of the hydrogen-bonded OH groups serve as bonding sites to Ti-isopropoxide. ZrCl<sub>4</sub> pulsed straight after Ti-isopropoxide binding without HCl treatment between the pulses removes part of the Ti from the surface.

**Table 2B. Binding of Ti and Zr on SiO<sub>2</sub> from Ti-isopropoxide and ZrCl<sub>4</sub>.**

Sample	Pretreatment T °C/h	Reaction T °C/h	Concentration (wt-%)			
			Zr	Ti	Cl	C
30	300/16+3	Zr 300/2	5.9	0.6	1.9	<0.1
31	300/16+3	Ti-i 210/2	7.7	0.3	3.8	<0.1
32	300/16+3	Zr 300/2	7.3	3.3	6.4	<0.1
		Ti-i 210/2				
		HCl 210/2				
		Ti-i 210/2				
		HCl -->300/ 1.5				
		Zr; 300/2				
33	300/16+3	Ti-i 210/2	7.7	1.7	5.8	<0.1
34	300/16+3	Zr 300/2	7.8	0.6	6.0	<0.1
		Ti-i 210/2	-	3.5	2.9	0.2
		HCl 210--> 300/1	-	3.3	2.9	0.2
35	300/16+3	Ti-i 200/2	10.3	0.76	7.4	<0.1
		Zr 200--> 300	9.3	0.73	7.9	<0.1

**Example 3. Polymerization of ethylene**

Polymerizations were carried out under the conditions described in section B above. The results are indicated in Table 3.

**Table 3. Polymerization of ethylene with ZrCl<sub>4</sub>/silica or alumina catalysts at 95 °C and 31 bar**

5	Sample No.	1	2	3	4	5
	Support pretreatment °C	300	300	300	450	800
	Zr load/wt-%	6.8	6.6	10.9	6.5	3.6
10	Run time/min.	60	60	60	60	60
	Catalyst amount/mg	166	158	179	170	171
	Cocatalyst/ml	2	2	2	2	2
	Al/Zr ratio	10	11	6	10	18
15	H <sub>2</sub> (bar)/500 ml	5	5	5	5	5
	Yield/g PE	101	52	86	64	49
	Activity					
	g PE/g cat h	608	329	536	376	287
	g PE/g Zr h	8,948	4,987	4,917	5,837	8,072
20	BD g/cm <sup>3</sup>	0.45	0.44	0.26	0.26	0.26
	MFR <sub>21.6</sub>	0.1	0.3	0.0	0.0	0.0

When a cocatalyst was fed to the polymerization, maximum activities were obtained at low Al/Zr ratios. Figure 3 shows the activity as a function of the Al/Zr molar ratio. The cocatalyst did not change the polymer MFR<sub>21.6</sub> values. The influence of hydrogen to catalyst activity was also evaluated. It appeared that the MFR<sub>21.6</sub> values of the produced polymers grew as the ratio H<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> increases. The weight average molecular weight ( $M_w$ ) decreased from 416,000 to 315,000 as the ratio was raised. Hydrogen broadened the molecular weight distribution, and the polydispersity increased from 15 to 21. A bimodal distribution was also observed, as indicated by Figure 6.

Two ZrCl<sub>4</sub>/silica catalysts, whose supports had been pretreated at 600 or 750 °C and having Zr concentrations of 3.4 and 2.0 wt-%, respectively, were also tested for catalytic activity. It

appeared that they were not at all active in the polymerization of ethylene.

**Example 4. Catalyst modification with Al-alkyl-compounds**

5

Table 4 presents the polymerization results using three different Al-alkyls for modifying the activity of catalyst No. 2 of Example 1. Using TEA as a modifier, the activity increased remarkably from 330 to 750 g PE/g cat h compared to the normal run with cocatalyst. When trimethylaluminium (TMA) was used as a modifier, activity was further increased to 1,230 g PE/g cat h. Also, MFR<sub>21.6</sub> increased a little. Diethylaluminium methoxide (DEALOX) changed MFR<sub>21.6</sub> values considerably, but not the catalyst activity. The ethoxide group could have some kind of different effect on the termination process.

15 **Table 4. Modification of catalyst with Al-alkyl-compounds**

Sample No.	2	2	2	2
Run time/min	60	60	60	60
Catalyst amount/mg	158	150	158	165
Cocatalyst/ml	2	-	-	-
Al/Zr ratio	11	2.6 DEALOX	2.4 TEA	2.6 TMA
H <sub>2</sub> (bar)/500 ml	5	5	5	5
Yeild/g PE	52	51	118	203
Activity g PE/g cat h	329	340	747	1,230
g PE/g Zr h	4.987	5,152	11,318	18,636
BD g/cm <sup>3</sup>	0.44	0.42	0.31	0.40
MFR <sub>21.6</sub>	0.3	2.6	0.5	0.9

30

**Example 5. Catalyst modification with Al-alkyl-compounds**

Further preactivation tests with aluminium alkyl compounds were carried out for Ti-modified catalysts. The polymerization results are indicated in Table 5.

5

**Example 6. Copolymerization and polymer properties**

10 Copolymerization of ethylene with 1-hexene was carried out using TMA preactivated  $\text{ZrCl}_4/\text{SiO}_2$  catalysts. The comonomer was added as a batch to the hot reactor simultaneously with the ethylene and hydrogen. The polymerization conditions and results, including the effect of polymerization temperature and comonomer on melting point, crystallinity and crystallization temperature are indicated in Table 6.

15 The comonomer incorporation was about 1 wt-%, according to NMR results. 1-hexene did not affect the activity in cocatalyst run, but its effect on  $M_w$  was clear. The comonomer lowered the melting point from 133.3 °C to 130.1 °C; crystallinity and crystallization temperature were lower with comonomer.

Table 5. Polymerization results of Zr, Ti/SiO<sub>2</sub>-catalysts. Silica pretreated at 300 °C. Run conditions: T=95 °C, p<sub>tot</sub> = 3100 kPa, H<sub>2</sub> 500 kPa/500 cm<sup>3</sup> and medium isobutane 1.8 cm<sup>3</sup> (Zr=ZrCl<sub>4</sub>, Ti=TiCl<sub>4</sub>, Ti-i=Ti(i-OPr)<sub>3</sub>).

Sample	6	6	8	12	13	10	10	14	14	15
Preparation	Zr300	Zr300	Ti175	Zr300 Ti-i210 HCl210	Ti-i210 HCl210 Zr300	Zr300 Ti250	Zr300 Ti250	Ti250 Zr300	Zr300 Ti-i200 HCl Zr300	Ti-i200 HCl Zr300 N <sub>2</sub> 600 Ti-i200 HCl Zr300
Analysis, Zr wt-%	6.9	6.9	-	7.7	7.3	5.9	5.9	9.3	10.9	10.0
Ti wt-%	-	-	3.8	0.3	3.3	1.0	1.0	<0.1	2.4	1.4
Cl wt-%	-	-	6.9	3.8	6.4	6.3	6.3	6.7	6.1	4.0
C wt-%	-	-	-	<0.1	<0.1	-	-	-	<0.1	<0.1
Cocatalyst	TEA	-	TEA	TEA	TEA	TEA	TEA	TEA	-	TEA
Preactivation	-	TMA	-	-	-	-	TMA	-	TMA	-
Al/M	10	2.5	57	8	12	13	4.1	11	3.1	4.5
Activity gpPE/gcat/h	290	900	60	70	210	140	580	230	860	160
MRF <sub>21,6</sub>	0.3	0.9	5.0	0.1	0.3	0.3	0.3	0.4	1.2	0.6

Table 6. Copolymerizations with 1-hexene using Zr/SiO<sub>2</sub> (sample 6) -catalysts. Polymerization conditions: T = 95 °C and 3100 kPa. Al/Zr = 10 during cocatalyst runs and 2.5 during preactivation.

Cocatalyst runs (TEA)	Comon. ml	Activity kgPE/gcat/h	Hexene in pol. wt-%	M <sub>w</sub> *10 <sup>6</sup>	SCE	UCE	T <sub>m</sub> °C	Cryst. %	T <sub>cr</sub> °C
A	-	0.29	-	1.6	-	-	-	-	-
B	50	0.29	0.2	1.4	1.4	0.5	-	-	-
Preactivated catalysts (TMA)									
C	-	0.90	-	1.2	3.1	1.8	133.3	72.9	117.7
D	50	0.77	0.8	0.8	4.2	3.7	130.1	67.1	115.1
E <sup>a)</sup>	-	1.62	-	0.9	2.1	1.7	133.4	68.8	116.7

a) Temperature 105 °C and pressure 3500 kPa. SCE = saturated chain ends/1000 C (NMR),

UCE = unsaturated chain ends/1000 C (NMR),

T<sub>m</sub> = polymer melting point (DSC),

T<sub>cr</sub> = polymer crystallization temperature (DSC),

Cryst. = crystallinity (DSC).

**Example 7. Modification of the support with an organic aluminium compound**

Zr-catalyst were prepared by vaporizing  $\text{ZrCl}_4$  at 270 °C and TMA at room temperature and binding the compounds from vapor phase to a silica support (Grace 955). The following  
 5 tables indicate the reaction conditions, including the order of introduction of the reagents, and the elemental concentrations of the catalysts (Table 7) as well as the results of polymerization of ethylene (Table 8).

**Table 7. Preparation of catalysts**

10

Sample	Preheat (°C/h)	Reaction (°C/h)	Zr (wt-%)	Al (wt-%)	Cl (wt-%)	C (wt-%)
35	300/16+3	$\text{ZrCl}_4$ 300/2	7.1	-	7.0	-
36	600/16 + 450/3	TMA 80/4 $\text{ZrCl}_4$ 300/2	4.7	2.7	6.2	nd
37	300/16+3	$\text{ZrCl}_4$ 300/2 TMA 80/4	6.8	1.8	5.9	1.4
15 38	300/16+3	TMA 80/4 $\text{ZrCl}_4$ 300/2	5.0	3.4	6.7	0.9

**Table 8. Polymerization results**

20

Sample	Al:Zr	T polym. °C	$\text{H}_2$ ml/bar	Activity kg PE/g/h
35	60*	95	-	0.32
36	0.9	70	80	0.16
25 37	0.9	95	-	0.40
38	2.3	95	-	-

\* cocatalyst added (1.5 ml 30 % MAO), other samples did not contain cocatalyst



**CLAIMS:**

1. A process for preparing a heterogeneous catalyst for polymerization of olefins, said catalyst comprising at least one group IVa metal compound on a solid inorganic oxidic support, comprising:
  - a) vapourizing at least one solid group IVa metal halide compound;
  - b) routing the vapour of said metal halide compound into a reaction chamber, wherein said vapour is reacted with said support at about 250 to about 500 °C in order to bind said metal halide compound to said support;
  - c) removing any metal compound not bound to said support as well as any volatile reaction products emanating from the reaction between said metal halide compound and said support from said reaction chamber in the vapour phase; and
  - d) optionally treating the product obtained from reacting said metal halide compound and said support with an organic aluminum compound to increase the catalytic activity of said catalyst.
2. The process according to claim 1, wherein steps a) to c) are repeated at least once using a halide of another group IVa metal compound.
3. The process according to claim 1, wherein said product obtained from the reaction between said metal halide compound and said support is treated with a titanium compound in order to modify the catalytic properties of said catalyst.
4. The process according to claim 1, wherein said group IVa metal halide compound is selected from the group consisting of a chloride and a bromide of zirconium or hafnium.
5. The process according to claim 4, wherein said chloride of zirconium is  $\text{ZrCl}_4$ .

6. The process according to claim 4, wherein said chloride of hafnium is  $\text{HfCl}_4$ .
7. The process according to claim 1, wherein a silica support is used and step b) is carried out at a temperature of 250 to 350 °C in order to produce a catalyst comprising an  
5 amorphous group IVa metal compound on a silica support.
8. The process according to claim 1, wherein the vapour pressure of said group IVa metal halide compound is maintained sufficiently high and the duration of the reaction with said support material is sufficiently long so as to provide at least an equal amount of said metal  
10 halide compound with respect to the number of available bonding sites of said support.
9. The process according to claim 1, wherein, prior to step a), the surface of said support is modified by reacting said support with an aluminum compound.
- 15 10. The process according to claim 1, wherein, subsequent to step c), said catalyst is preactivated with a compound selected from the group consisting of TMA, TEA, TIBA, DEA, MAO, and DEALOX in order to increase its activity .
11. The process according to claim 10, wherein the preactivating is carried out in a liquid  
20 phase.
12. The process according to claim 1, wherein said reaction chamber is purged with nitrogen in step c).
- 25 13. The process according to claim 1, wherein step b) is carried out at a temperature of from about 260 to about 320 °C.
14. A heterogeneous catalyst for polymerization of one or more olefins, optionally in the presence of a cocatalyst, comprising at least one group IVa metal compound on a solid oxidic  
30 support, wherein said group IVa metal compound is a Zr or Hf compound deposited on said support from the vapour phase.

15. The catalyst according to claim 14, further comprising an aluminum alkyl compound selected from the group consisting of TMA, TEA, TIBA, DEA, MAO, and DEALOX.

16. The heterogeneous catalyst according to claim 14, wherein:

5       said group IVa metal compound is amorphous and has the formula  $ZrY_x$ ,  
      wherein Y is halo and x is 2 or 3;

      said support comprises a compound selected from the group consisting of silica  
      and alumina; and

10

      said catalyst catalyzes homo- or copolymerization of ethylene at a pressure of  
      at least 500 kPa, producing polyethylene having a broad molecular weight  
      distribution.

15 17. The catalyst according to claim 14, further comprising at least one titanium compound.

18. A process for polymerization of olefins in order to produce a polymer having a broad  
molecular weight distribution, comprising contacting, in one or more polymerization reactors  
in the slurry or gas phase, olefin monomers or mixtures thereof at an increased pressure of at  
20 least 500 kPa with a heterogeneous catalyst comprising at least one group IVa metal  
compound on a solid inorganic oxidic support, wherein said group IVa metal compound is a  
Zr or Hf compound deposited on said support from the vapour phase.

19. The process according to claim 18, wherein said polymerization is carried out at a partial  
25 hydrogen pressure of at least 10 kPa.

20. The process according to any one of claims 18 or 19, wherein a cocatalyst is fed into the  
polymerization reactor separately or together with said catalyst.

30 21. The process according to claim 20, wherein said cocatalyst is selected from the group  
consisting of TMA, TEA, TIBA, DEA, MAO, and DEALOX.

22. The process according to claim 18, wherein said olefin monomer is ethylene, and said polymer is polyethylene having a bimodal molecular weight distribution.

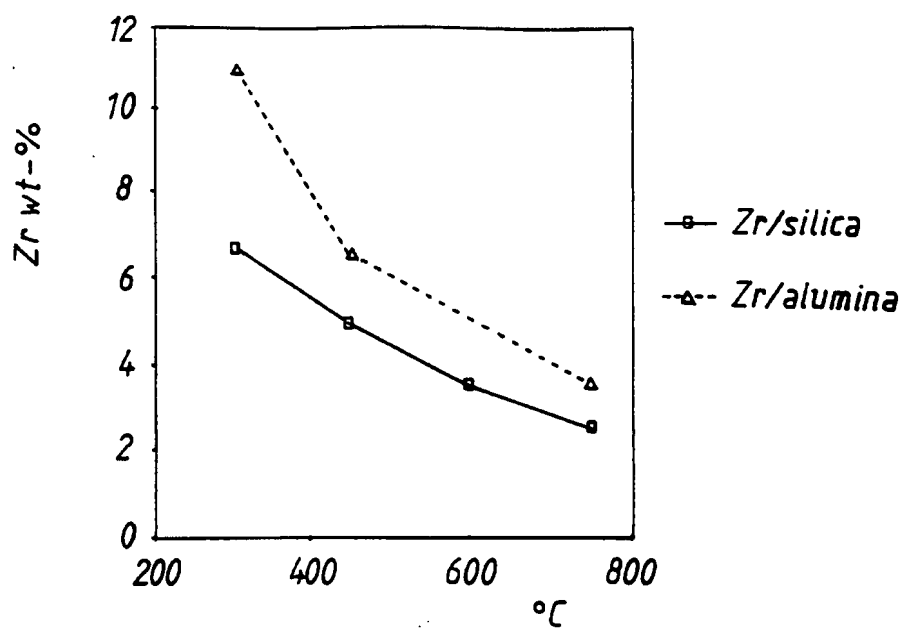


Fig. 1

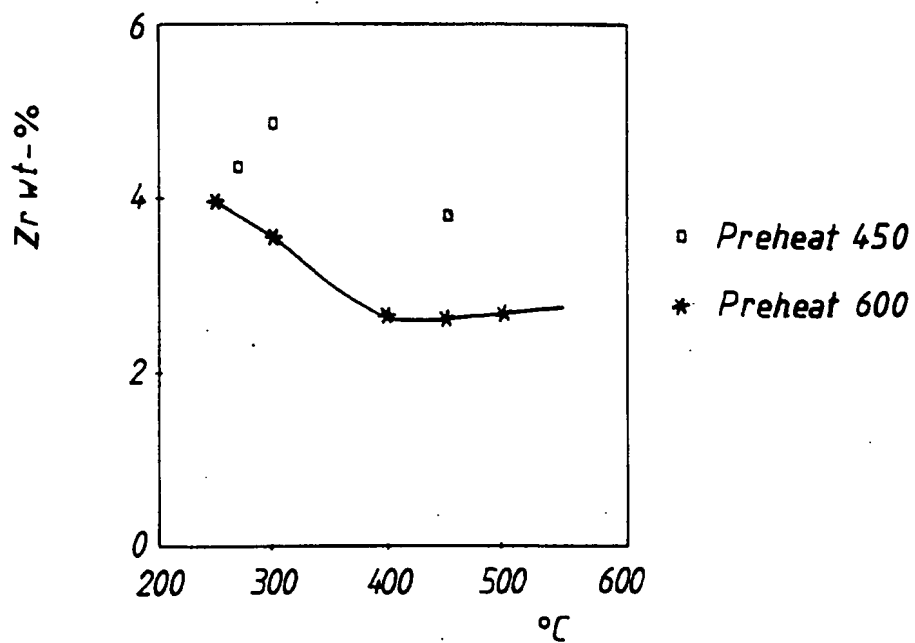
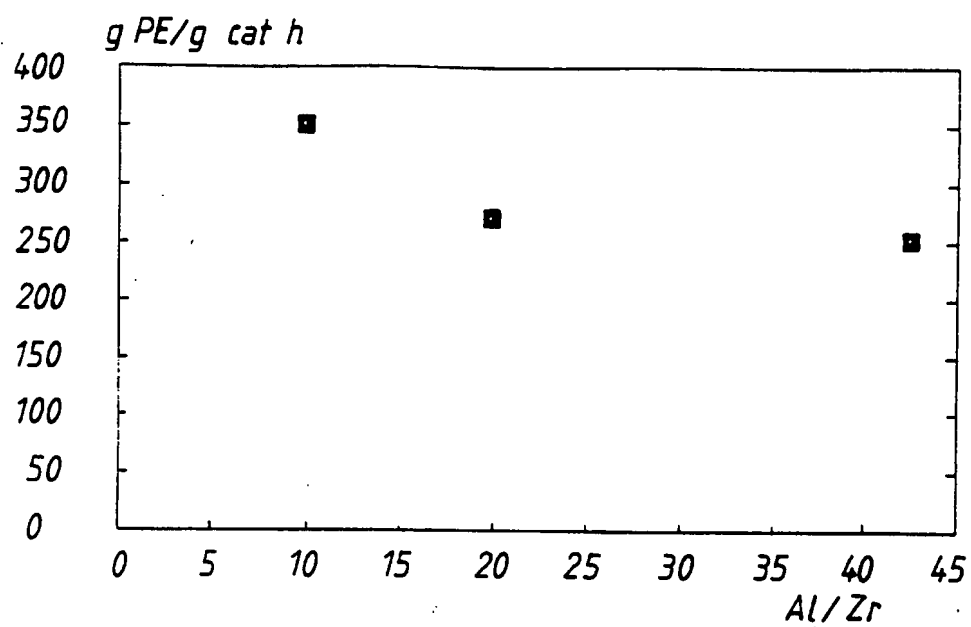
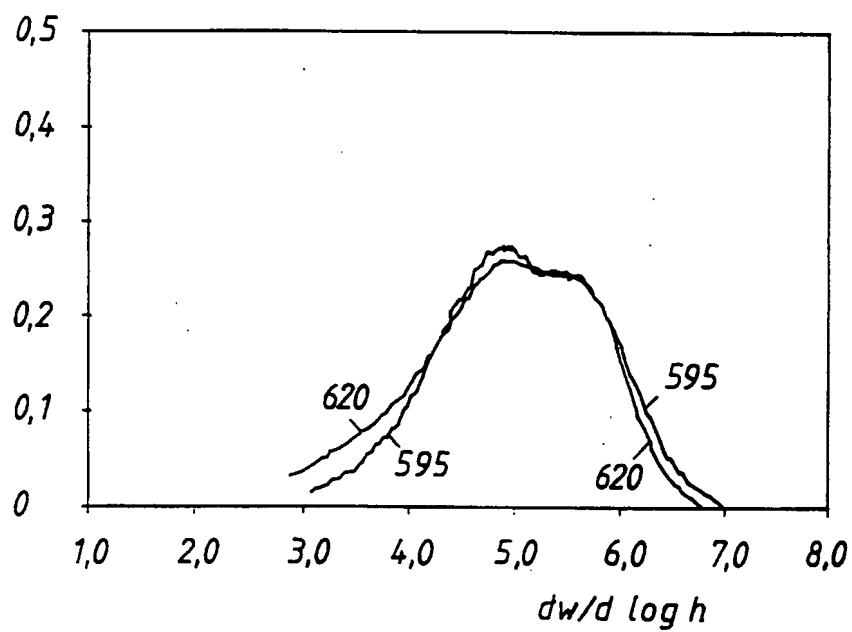
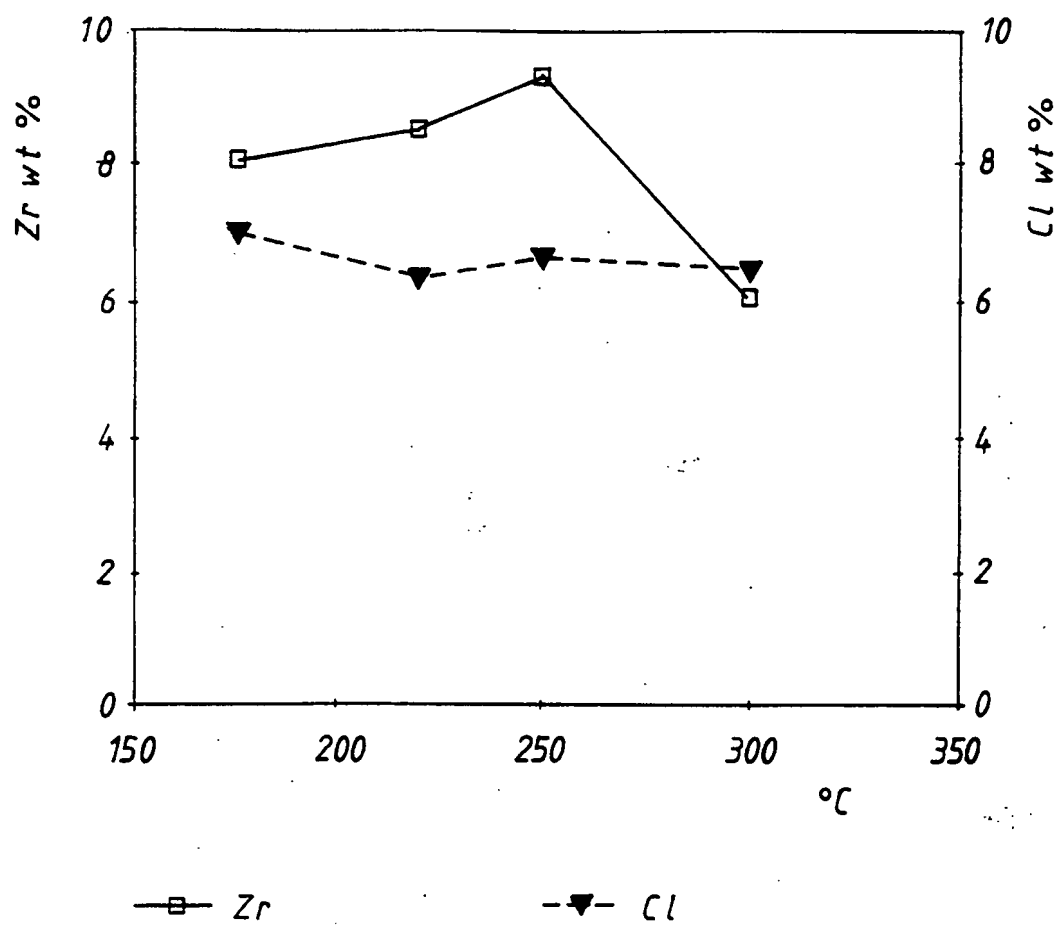


Fig. 2

*Fig. 3**Fig. 6*

*Fig.4*

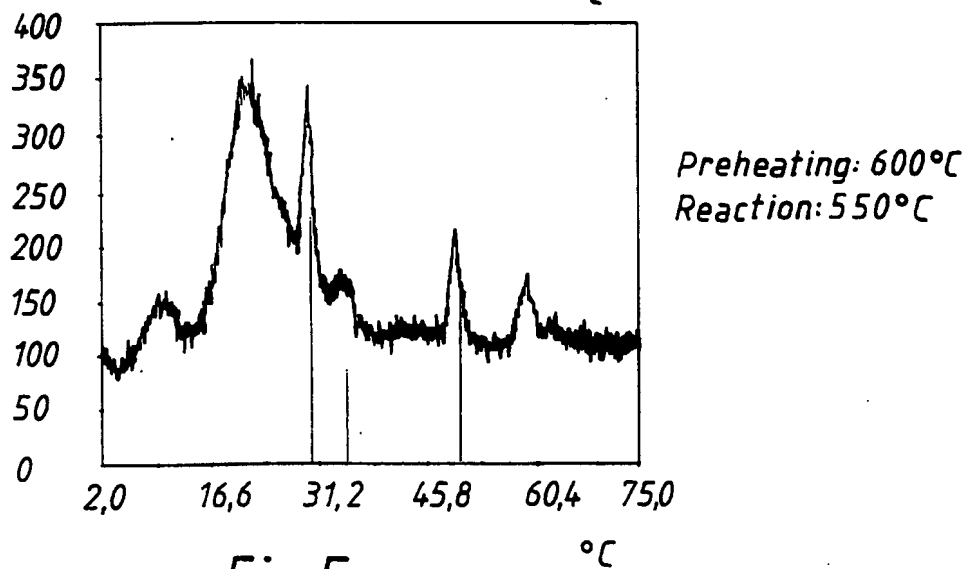
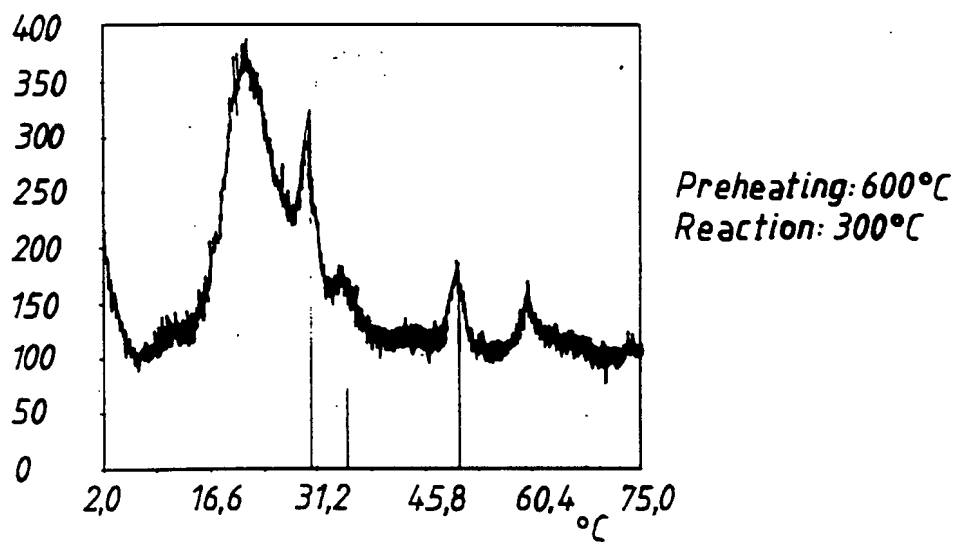
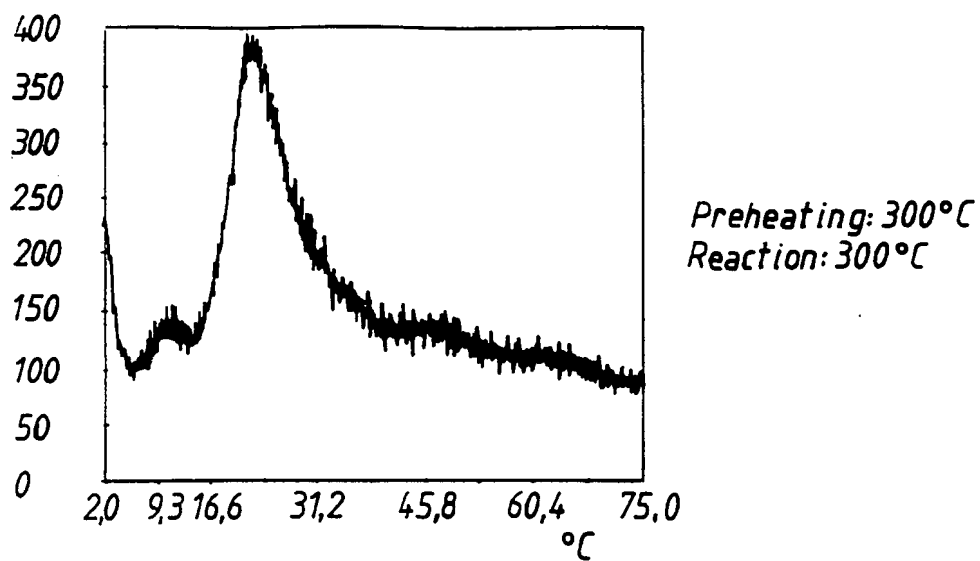


Fig.5



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 94/00394

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08F 4/16, C08F 10/00, B01J 37/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08F, B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPIL

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 4459372 (BLAISE J. ARENA), 10 July 1984 (10.07.84), column 3, line 9 - column 4, line 13, claim 1	1-8,12-14,17
Y	--	9-11,15,16,18-22
Y	US, A, 5070055 (KATHLEEN D. SCHRAMM ET AL), 3 December 1991 (03.12.91), column 7, line 64 - column 8, line 50; column 10, line 68 - column 11, line 2; column 16, line 5 - line 19, tables	9-11,15,16,18-22
	--	

☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

## \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

15 December 1994

Date of mailing of the international search report

19-12-1994

Name and mailing address of the ISA/

Swedish Patent Office

Box 5055, S-102 42 STOCKHOLM

Facsimile No. +46 8 666 02 86

Authorized officer

Hans Bäckström

Telephone No. +46 8 782 25 00

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 94/00394

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, A2, 0438132 (NESTE OY), 24 July 1991 (24.07.91)  -----  -----	1-22

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

26/11/94

International application No.  
PCT/FI 94/00394

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US-A-	4459372	10/07/84	NONE		
US-A-	5070055	03/12/91	AU-B-	636771	06/05/93
			AU-A-	7943891	02/01/92
			CA-A-	2045967	30/12/91
			CN-A-	1058601	12/02/92
			EP-A-	0464710	08/01/92
			JP-A-	4226509	17/08/92
EP-A2-	0438132	24/07/91	JP-A-	6211913	02/08/94
			US-A-	5290748	01/03/94